

ORNL MASTER COPY

ORNL/M-1030

OAK RIDGE NATIONAL LABORATORY

MARTIN MARIETTA

Mercury Monitoring of Water and Sediment in Oak Ridge National Laboratory Streams During 1989

Fred G. Taylor, Jr.

hem Risk Document No. 162

AGED BY TIN MARIETTA ENERGY SYSTEMS, INC. THE UNITED STATES RTMENT OF ENERGY This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

NTIS price codes—Printed Copy: A03 Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MERCURY MONITORING OF WATER AND SEDIMENT IN OAK RIDGE NATIONAL LABORATORY STREAMS DURING 1989

Fred G. Taylor, Jr.

Environmental and Health Protection

Date Published: January 1990

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
operated by
Martin Marietta Energy Systems, Inc.
for the
U.S. Department of Energy
under Contract No. DE-AC05-840R21400

The assistance of D. F. Copeland, B. J. Hendrix, B. H. Freels, S. R. Lewis, J. L. Malone, D. W. Parsons, and J. B. Watson (Environmental and Health Protection Division) is gratefully acknowledged for sample collection. The Analytical Chemistry Division under the guidance of T. Shope provided the analytical chemistry services.

٥

.

	Contents	<u>Page</u>
LIST	OF FIGURES	vii
LIST	OF TABLES	ix
1.0	INTRODUCTION	1
2.0	AREA RECEIVING STREAMS	1
3.0	MERCURY SOURCES (SPILLS)	1
4.0	SAMPLE COLLECTION	8
5.0	SAMPLE PROCEDURE, DATA MANAGEMENT, AND CONTROL	8
	5.1 ANALYTICAL METHODS	8
	5.2 DATABASE MANAGEMENT SYSTEM	8
	5.3 QUALITY ASSURANCE	8
	5.3.1 SAMPLE ANALYSIS	8
	5.3.2 REPLICATE SAMPLES	9
	5.3.3 CHAIN OF CUSTODY	9
6.0	RESULTS	9
	6.1 WATER	9
	6.1.1 FIRST QUARTER SAMPLING	9
	6.1.2 FOURTH QUARTER SAMPLING	13
	6.2 SEDIMENT	13
	6.2.1 FIRST QUARTER SAMPLING	13
	6.2.2 FOURTH QUARTER SAMPLING	19
	6.2.3 OUTFALL 261 AND OUTFALL 362	19
7.0	CONCLUSIONS AND RECOMMENDATIONS	23
0 0	REEDENOCE	27

• .

LIST OF FIGURES

<u>Figu</u>	<u>re</u>						<u>Page</u>
1	Sampling stations in the ORNL Bethel Valley Complex . The circled numbers are positioned as near as possible to the outfalls.		•	•	•	•	2
2	Sampling stations in the ORNL Melton Valley Complex . The circled numbers are positioned as near as possible to the outfalls.	•	•	•	•	•	3
3	Location of ORNL streams, rivers, and impoundments	•	•	•	•	•	4
4	Locations in ORNL streams with excess mercury in sediments. Statistics are summarized in Table 4. Data represent first quarter 1989 sampling.	•	•	•	•	•	17
5.	Locations in ORNL streams with excess mercury in sediments. Statistics are summarized in Table 5. Data represent fourth quarter 1989.	•	•	•	•	•	20
6	Mercury concentrations along a distance gradient below Outfall 261 to a depth of 20 cm.	•	•	•	•	•	22

LIST OF TABLES

Table		<u>Page</u>
1	Summary of Known Mercury Spills at ORNL	5
2	Summary of Analytical Data (Water) for the	10
3	Summary of Analytical Data (water) for the	14
4	Summary of Mercury Concentrations (ug/g \pm 1 SE) in Sediments from ORNL Streams, First Quarter 1989	18
5	Summary of Mercury Concentrations (ug/g \pm 1 SE) in Sediments from ORNL Streams, Fourth Quarter 1989	21
6	Outfalls Recommended for Continued Water Sampling by Stream or Outfall	24
7	Location Recommendations for Continued Sediment	25

1.0 INTRODUCTION

An assessment plan was implemented in compliance with the Clean Water Act and the Oak Ridge National Laboratory's (ORNL) National Pollutant Discharge Elimination System (NPDES) Permit to identify, locate, and minimize all sources of mercury contamination in ORNL discharges to the aquatic environment. This plan was designed to identify sources of mercury from past operations and spills through a review of file records and personal interviews. A network of monitoring and sampling stations, based on knowledge of mercury deposits in receiving streams, knowledge of mercury discharges from pipes to streams, and a review of chemical data from previous contaminant surveys, was established for sample collection. The plan was designed to assess the potential for mercury reaching surrounding streams and rivers by placement of sampling sites relative to potential contaminant movement from areas of deposition. This summary report describes the monitoring data for 1989, collected during the first and fourth quarters, while contrasting to the 1988 data. Based on 1988-1989 data, recommendations are proposed to eliminate those sample locations which have not provided quantitative evidence of mercury deposition. Sample locations near sources identified from the monitoring data will be retained in the sample network.

2.0 AREA RECEIVING WATERS

Effluents from the numerous laboratories at ORNL are treated and subsequently monitored before discharging into the receiving streams at permissible concentrations. In previous years, before stringent regulations, some contaminants reached various streams primarily as the result of accidental spills or leaks. The intent of the monitoring effort is to provide evidence that no new sources of mercury have resulted from plant operations. Receiving streams within the ORNL perimeter include White Oak Creek, Fifth Creek, First Creek, and Northwest Tributary. The more remote streams, Melton Branch, White Oak Lake, Clinch River-Melton Hill Reservoir, and Clinch River-Watts Bar Reservoir systems also receive effluents from plant operations. The locations of area streams and reservoirs are depicted in Figs. 1, 2, and 3.

3.0 MERCURY SOURCES (SPILLS)

Two major uses of mercury at ORNL involved pilot plant operations in 1954-1955 supporting the thermonuclear weapons program at Y-12. Both activities involved separation processes in Buildings 4501 and 4505. At the time of the operations, an unknown number of mercury spills occurred. Although these spills were cleaned up, it is evident from soil analyses around the buildings that quantities of mercury escaped and reached the environment (Oakes, 1983a,b). Key individuals with personal knowledge of the operations were interviewed concerning the history of mercury spills, and a tabulation of reportable chemical spills at ORNL involving mercury was summarized (Table 1) to August 1989 (Alexander, 1989).

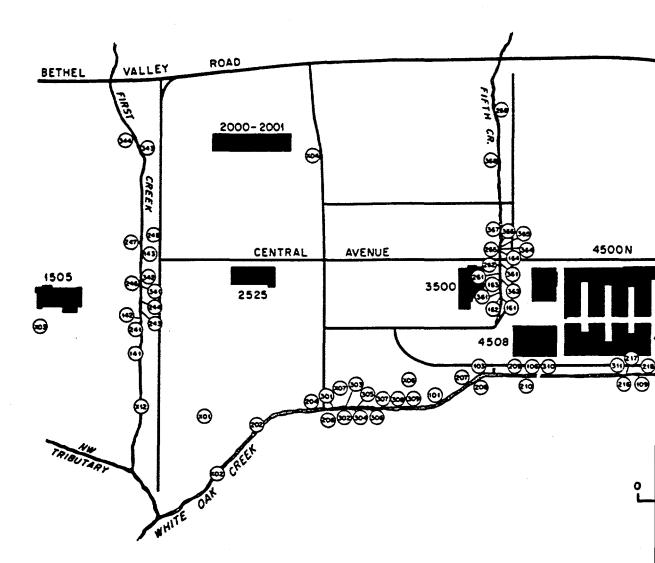
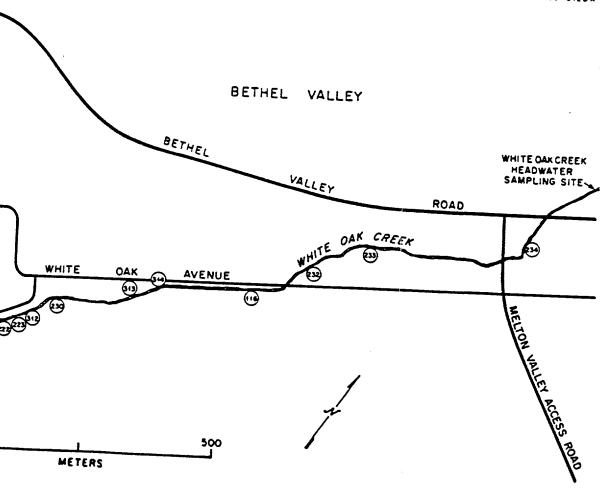
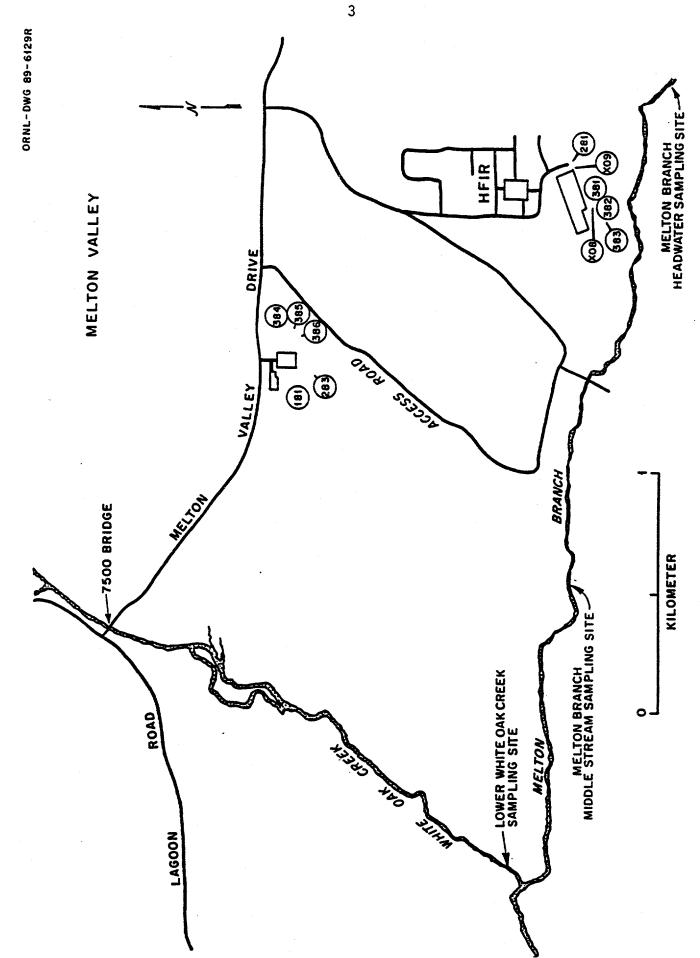


Fig. 1. Sampling stations in the ORNL numbers are positioned as near

ORNL-DWG 89-6128 R



el Valley Complex. Circled possible to the outfall location.



Sampling stations in the ORNL Melton Valley Complex. The circled numbers are positioned as near as possible to the outfall locations. Fig. 2.

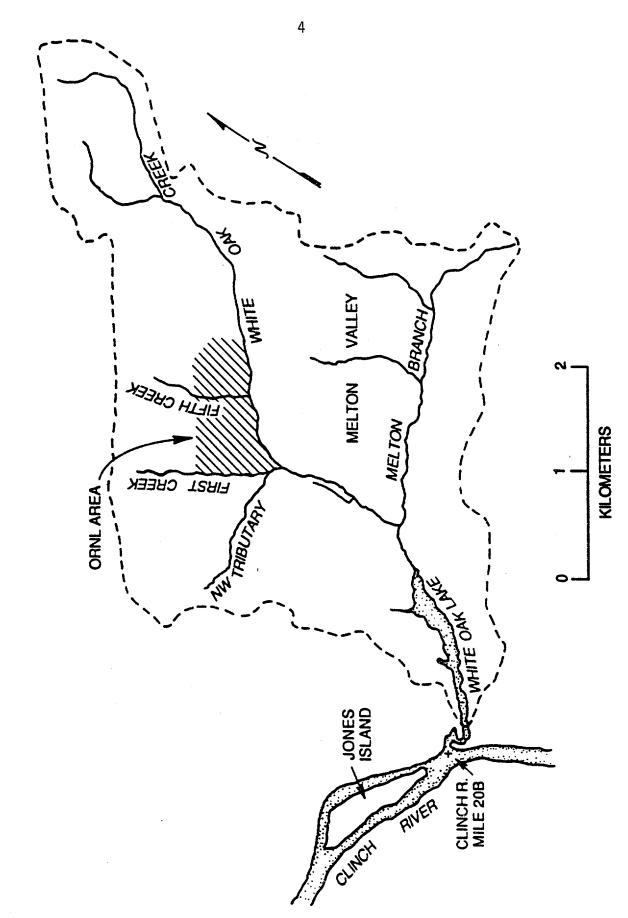


Fig. 3. Locations of ORNL streams, rivers, and impoundments.

Table 1. Summary of Known Mercury Spills at ORNL

	•		• •	
Building	Process	Year	Amount	Outfall -
4501	Lithium isotope separation	1954	>23,000 kg	362, 363
4505	Uranium and thorium metal production	1955	2,000 kg	362,363
3592	Mercury cleaning	1963	5,000 kg	207
3503	Mercury flask and clean mercury storage	1963	unknown	207
2525	Spill	1981	1.5 kg	103,207, 208
4500S	Spill	1980	<1.0 kg	109.217 218.311
3500	Spill	1981	<0.02 kg	163,162 207,261 361
4500N	Spill	1984	<0.02 kg	X06,309
Fifth Creek	Spill	1985	<0.02 kg	362
4500N	Spill	1985	<0.02 kg	263,309, X06
1505	Spill	1985	<0.02 kg	241,NWT
4500S	Spill	1985	0.03 kg	109,217 218,309 311,X06
4500N	Spill	1985	6.5 kg	263,309 X06
4500S	Spill	1985	<0.02 kg	109,217 218,311 309,X06
6000	Spill	1985	<0.02 kg	263,309
				X06

6
Table 1 (cont.)

5.17.11		V		0.46-11
Building	Process	Year	Amount	Outfall
4500S	Spill	1985	<0.02 kg	109,217 218,311 309,X06
4505	Spill	1986	<0.02 kg	161,362 363
3504	Spill	1986	0.9 kg	207,208 309,X06
3504	Spill	1986	0.112 kg	207,208 309,X06
4500N	Spill	1986	0.112 kg	263,309 X06
1506	Spill	1987	0.028 kg	241,X02 NWT
3500	Spill	1987	0.056 kg	162,163 261,262, 361
5505	Spill .	1987	0.1 kg	226,230 312
4500N	Spill	1987	<0.02 kg	263,309 X06
3504	Spill	1987	0.135 kg	207,208, 309,X06
3500	Spill	1987	0.084 kg	162,163 207,261 361
4501	Spill	1987	0.200 kg	362,363
4500S	Spill	1988	0.112 kg	109,217 218,311 309,X06
4508	Spill	1988	0.01 kg	106,107 109,209 210,217 309,310 311,X06

7
Table 1 (cont.)

Building	Process	Year	Amount	Outfall
3095	Spill	1988	0.01 kg	107,267 363
4501	Spill	1988	0.200 kg	263,362
1505	Spill	1988	0.020 kg	NWT
7567	Spill	1988	0.027 kg	none
4512	Spill	1988	0.994 kg	214,215 216
1505	Spill	1989	0.014 kg	NWT
4505	Spill .	1989	0.014 kg	161,362 363
3038	Spill	1989	0.027 kg	106,107 209,210 310
3012	Spill	1989	0.112 kg	166,266
3017	Spill	1989	0.280 kg	X04
4501	Spill	1989	0.056 kg	263,362 363
3500	Spill	1989	0.014 kg	162,163 261,262, 361
3095	Spill	1989	0.028 kg	5th Creek
2011	Spill	1989	0.406 kg	249,X04

4.0 SAMPLE COLLECTION

All water samples consist of three replicate, manual grab samples collected during two sampling periods (dry and wet seasons) during 1989. Samples were collected in 1-L I-Chem high-density polyethylene bottles with teflon caps. I-Chem bottles are proprietary containers, precleaned by the vendor to EPA specifications where microchemical determinations are requested. Samples were preserved immediately upon collection by acidifying with concentrated nitric acid to a pH of <2.0. Sediment samples were collected at selected stations and placed in glass containers. The glass containers were also I-Chem, EPA approved. Generally, samples were analyzed as soon as possible after collection, and no sample analysis exceeded the maximum allowable holding time of 28 days.

5.0 SAMPLE PROCEDURES, DATA MANAGEMENT, AND CONTROL

5.1 ANALYTICAL METHODS

Sediment samples were first extracted by utilizing SW845 methodology (USEPA, 1982). A modification of Method 245.1 (USEPA, 1983) was utilized for all analyses, and the results of sediment analyses were reported on a dry weight basis.

5.2 DATABASE MANAGEMENT SYSTEM

A computerized NPDES database exists on the Environmental Monitoring and Compliance Section's VAX computer. The database can be modified to maintain all records and allow for retrieval of records and data from all sampling and monitoring activities. The database permits tracking of all sampling sites and includes the date and time of collection, the identity of the individuals collecting each sample, and a description of how and under what conditions the sample was collected. Analytical data are transferred to the database by computer from entries verified by the laboratory supervisor in the Analytical Chemistry Division's computer. Hard copies also provide verification. The structure of the database is such that retrieval of information for risk assessment is possible.

5.3 QUALITY ASSURANCE

5.3.1 Sample Analysis

The validity of the sample analysis was demonstrated by the use of distilled water blanks to ensure that all glassware and reagents were interference-free. The blanks were carried through all stages of sample preparation and analysis. Blanks were used with each set of samples. All samples were analyzed within the prescribed time limit (28 days) noted previously.

5.3.2 Replicate Samples

Three replicate field samples were collected to ensure that the sampling techniques were consistent and to identify the concentration variability at each station. Laboratory duplicates within samples were analyzed to assure precision of analysis.

5.3.3 Chain of Custody

A "DOE X-10 Chain-of-Custody" form was completed and remained with the sample until the Analytical Chemistry Division assumed control of the sample. At that time, an "Analytical Chemistry Division Chain-of-Custody" form was initiated and remained with the sample until the analyses were completed. Any additional information or variation in standard procedures was noted in a laboratory notebook.

6.0 RESULTS

6.1 WATER

6.1.1 First Quarter Sampling

In March 1989, 91 stations were sampled for mercury content. Each site consisted of three replications for a total of 273 samples (Table 2). The lower detection limit for this series of samples was <0.05 ng/mL. Only fifteen locations identified quantitative concentrations (mean \pm 1 SE). Among those outfalls along Fifth Creek, Outfall 367 had a concentration of 3.03 \pm 0.34 ng/mL, a factor of three greater than noted in the spring of 1988. This outfall is east of Building 3039, Central Radioactive Disposal Facility. Outfalls 261 and 363 had >0.1 ng/mL concentrations; all others along Fifth Creek were below the detection limit.

Among 14 outfalls sampled along First Creek, none contained mercury at the detection limit (<0.05 ng/mL) in contrast to a single quantitative concentration of 0.5 ng/mL from Outfall 341 in the Spring of 1988 (Taylor, 1989).

Among 44 outfalls sampled along White Oak Creek in the first quarter, 12 contained mercury concentrations exceeding the detection limit. This is in contrast to 4 stations among 29 sampled during the same period of 1988. The highest concentration observed was 1.83 ng/mL from Outfall 304, a factor of 14 greater than observed from the same location during the same period last year. Outfall 304 is approximately 50 m east of the Process Waste Treatment Plant (Building 3544).

Along Melton Branch, no outfall among 11 stations had detectable mercury. Similarly, no station sampled in the Spring of 1988 had detectable mercury concentrations.

Miscellaneous stations (remote streams) sampled in 1988 identified mercury (0.17 ng/mL) at one location, Lower Section of White Oak Creek. This compares to no detectable mercury among the same sites during the first quarter of 1989.

Table 2. Summary of Analytical Data (Water) for the First Quarter 1989 Sampling Effort^{ab}

Outfall Number/Location	n	ng/mL ± 1 SE
	First Creek 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	
141	3	<0.05
142	3	<0.05
143	3	<0.05
241	3	<0.05
243	3	<0.05
244	3	<0.05
246	3	<0.05
247	3	<0.05
248	3	<0.05
341	3	<0.05
342	3	<0.05
343	3	<0.05
344	3	<0.05
X12	3	<0.05
	Fifth Creek	
161	3	<0.05
162	3	<0.05
163	3	<0.05
164	3	<0.05
261	3	0.25 <u>+</u> 0.1
262	3	<0.05
265	3	<0.05
268	3	<0.05
361	3	<0.05
362	3	<0.05
363	3	0.50 ± 0.1
362 363 364	3	<0.05
365	3	<0.05
366	3	<0.05
366 367 368	3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	3.03 ± 0.3
368	3	<0.05
X10	3	<0.05

11

Table 2 (cont.)

Outfall Number/Location	n	ng/mL ± 1 SE
outiall Number/Location	n	119/#L I 4 JL
	WHITE OAK CREEK	
101	3	<0.13 ± 0.03
103		<0.05
106	3	<0.05
109	3	<0.05
116	3	<0.05
202	3 3 3 3	0.60 ± 0.06
204	3	<0.05
206	3	0.70 ± 0.21
207	3 3 3 3 3 3 3 3 3 3 3	0.16 ± 0.04
208	3	<0.05
209	3	<0.05
210	3	<0.05
216	3	<0.05
217	3	<0.05
218	3	<0.05
222	3	<0.05
223	3	<0.05
230	3	<0.05
232	3	<0.05
233	3	<0.05
234	3	<0.05
301	3	0.50 ± 0
302	3	0.50 ± 0
303	3 3 3 3 3 3 3	<0.05
304	3	1.83 ± 0.73
305	3	0.07 ± 0.04
306	3	<0.05
307	3	<0.05
308	3	<0.05
309		0.60 ± 0.10
310	3	<0.05
311	3 3	<0.05
312	3	<0.05 <0.05
313	3 2	
314 75000	ა ე	<0.05
7500B	3	<0.05 0.10 ± 0
Flume XOI	3	<0.05
X01 X02	3 3 3 3 3 3 3 3 3 3	<0.05
X02 X03	3	<0.05
X04	3	0.10 ± 0
X06	3	0.80 ± 0
X07	<u>~</u>	<u> </u>
White Oak Dam	<u>۲</u>	<0.05
MILLE VAK DANI	.	70.03

12
Table 2 (cont.)

Outfall Number/Location	n	ng/mL ± 1 SE
	MELTON BRANCH	
181		<0.05
281	3 3 3 3 3 3 3 3	<0.05
283	3	<0.05
381	3	<0.05
382	3	<0.05
383	3	<0.05
384	3	<0.05
385	3	<0.05
386	3	<0.05
X08	3	<0.05
Х09	3	<0.05
D. J. L. L.	<u>MISCELLANEOUS</u>	
Headwaters Melton Branch	3	<0.05
Headwaters White Oak Creek	3	<0.05
Lower White Oak Creek	3	<0.05
Melton Branch Small Mid Stream	3	<0.05
Melton Hill Dam Melton Branch	3	<0.05

 $^{^{\}rm a}{\rm Data}$ noted as < indicates mercury was not present at the detection limit (0.05 ng/mL).

 $^{^{\}mbox{\scriptsize b}}\mbox{\scriptsize Data}$ in boxes represent significant concentrations.

6.1.2 Fourth Quarter Sampling

In November of 1989, 88 stations were sampled for mercury content. Each site consisted of three replications for a total of 264 samples (Table 3). The lower detection limit for this series of samples was <0.05 ng/mL. locations identified quantitative concentrations (mean ± 1 SE). Among those outfalls along Fifth Creek, Outfalls 261 and 363 exceeded the analytical detection limit with concentrations of 0.12 \pm 0.08 and 0.10 \pm 0.003 ng/mL, respectively. During the first quarter, these outfalls did not have detectable Outfall 261 is east of Building 3500 and Outfall 363 is west of Building 4501. Among 13 locations along First Creek, only Outfall 341 exceeded analytical detection limits (0.37 \pm 0.01 ng/mL). During the first quarter, no outfall along First Creek had detectable mercury. Forty-five locations were sampled along White Oak Creek during the fourth quarter, with 17 showing detectable concentrations of mercury. This compares to 12 locations among 44 during the first quarter sampling. The maximum concentration (0.40 \pm 0.02 ng/mL) 304, observed from Outfall while the minimum concentration $(0.04 \pm 0.0]$ ng/mL) was from Outfall 210. Outfall 304 had the maximum concentration of 1.83 \pm 0.73 ng/mL during the first quarter. Outfall 304 is located south of the Process Waste Treatment Plant (Building 3544) and the Process Waste Water Treatment Plant (Building 3518). Nine locations were sampled along Melton Branch during the fourth quarter. Mercury was not detectable at any location. This was also the situation during the first quarter. Among miscellaneous locations (remote streams, background locations, etc.) the lower White 0ak Creek reported a quantitative concentration While this concentration is less than the analytical $(0.04 \pm 0.02 \text{ ng/mL}).$ detection limit, the standard error (50%) indicates that one or more replications had a detectable concentration. During the spring quarter none of the miscellaneous locations had detectable mercury.

6.2 SEDIMENT

6.2.1 First Quarter Sampling

Twelve stations were sampled for sediments along the Laboratory's streams at the same locations as in 1988. The 1988 report identified mercury in sediments ranging from 0.13 \pm 0.02 ug/g (White Oak Creek headwaters) to a maximum of 4874 \pm 2556 ug/g near Outfall 261, east of Building 3500. During the first quarter 1989 sampling effort, the same locations continued to exhibit elevated mercury concentrations. Outfall 261 had a mean of 555.67 \pm 310.38 ug/g, a factor of eight less than the concentration reported in 1988. The decrease is related to sampling variability and does not reflect a reduction of the source. A summary of the spatial mercury contamination of ORNL streams is presented in Fig. 4 and in Table 4. The data are not intended to infer a dilution with distance from the ORNL complex. For concentration data to be interpretated along a distance gradient to illustrate a dilution phenomenon, all sediments must be sieved with stones and organic materials removed. This was not the procedure with the sediments collected in this program.

The background concentration from White Oak Creek headwaters $(0.02 \pm 0.003 \text{ ug/g})$ is less than the average concentration (0.17 ug/g) reported for the eastern conterminous United States (Schacklette et al, 1971).

Table 3. Summary of Analytical Data (water) for the Fourth Quarter 1989^{a, b}

Outfall Number/Location	n	ng/mL ± 1 SE
	First Creek 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	
141	3	<0.05
142	3	<0.05
143	3	<0.05
241	3	<0.05
243	3	<0.05
244	3	<0.05
246	3	<0.05
247	3	<0.05
248	3	<0.05
341	3	0.37 ± 0.01
342	3	<0.05
343	3	<0.05
X12	3	<0.05
	FIFTH CREEK	
161	3	<0.05
162	3 3 3 3	<0.05
163	3	<0.05
164	3	<0.05
261	3	0.12 ± 0.08
262	3	<0.05
265	3	<0.05
268	3	<0.05
361	3	<0.05
362	3	<0.05
363	3	0.10 <u>+</u> 0.003
364	3 3 3 3 3 3 3 3 3 3	<0.05
365	3	<0.05
366	3	<0.05
367	3	<0.05
368	3	<0.05

Table 3 (cont.)

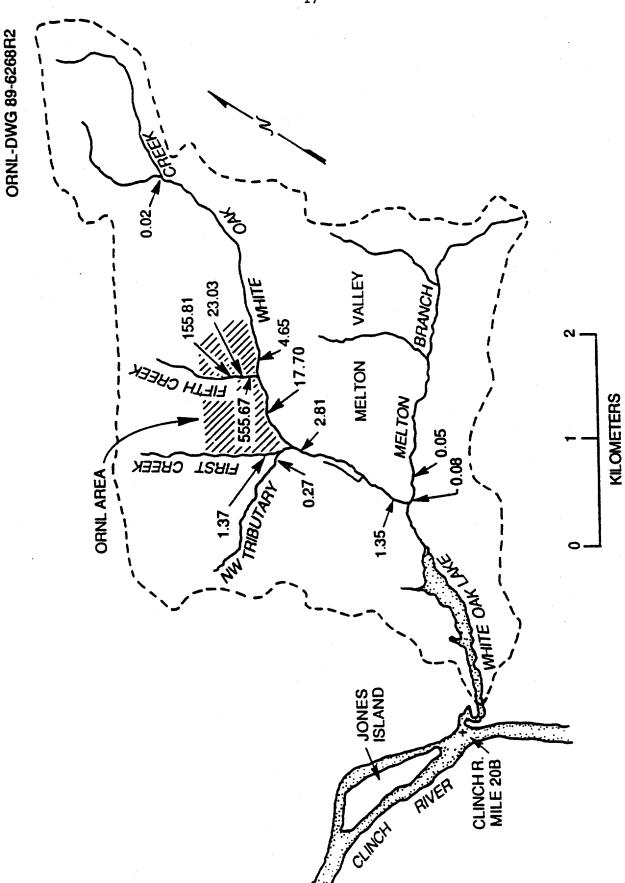
Outfall Number/Location	n	ng/mL ± 1 SE
	WHITE OAK CREEK	
101		<0.05
103	3 3	0.06 <u>+</u> 0.003
106	3	0.06 ± 0.01
109	3	<0.05
116	3	<0.05
202	3	<0.05
204	3	0.09 ± 0.01
206	3	0.07 ± 0.01
.207	3	<0.05
208	3 3	<0.05
209	3	0.15 ± 0.003
210	3	0.04 ± 0.01
216	3	<0.05
217	3	<0.05
218	3 3 3 3	<0.05
222	3	<0.05
223		<0.05
230	3	<0.05
233	3	<0.05
234	3	<0.05
301	3	0.07 ± 0.01
302	3	0.25 ± 0.02
303	3	0.15 ± 0.04
304	3	0.40 ± 0.02
305	3	<0.05
306	3	0.08 ± 0
307	3	<0.05
308	3	0.09 ± 0.01
309	3	0.10 ± 0.01
310	3	0.05 ± 0.003
311	3	<0.05
312	3	<0.05
313	3	<0.05
314	3	<0.05
7500 B	3 3	<0.05
FLUME	3	<0.05
WHITE OAK DAM	3	<0.05
X01	3	<0.05
X02	3	0.08 ± 0.01
X03		<0.05
· X04	3 3 3	<0.05
X06		<0.05
X07	3	0.14 ± 0.003
X11	3	0.10 ± 0

16
Table 3 (cont.)

Outfall Number/Location	n	ng/mL ± 1 SE	
	MELTON BRANCH		
181		<0.05	
281	3 3 3 3 3 3 3	<0.05	
283	3	<0.05	
381	3	<0.05	
382	3	<0.05	
383	3	<0.05	
384	3	<0.05	
386	3	<0.05	
Х09	3	<0.05	
	MISCELLANEOUS		
HEADWATERS MELTON BRANCH	3	<0.05	
HEADWATERS	3	<0.05	
WHITE OAK CREEK	•		
WHITE OAK CREEK LOWER CREEK	3	0.04 ± 0.02	
MELTON BRANCH MID SECTION	3	<0.05	
MELTON HILL DAM MELTON BRANCH	3	<0.05	

 $^{{}^{\}mathbf{a}}\mathsf{Data}$ in box represent significant concentration

 $[^]b\mathrm{Data}$ noted as < indicates mercury was not present at the detection limit (0.05 ng/mL)



Locations in ORNL streams with excess mercury in sediments. Statistics are summarized in Table 4. Data represent first 201 1000 actual Fig. 4.

Table 4. Summary of Mercury Concentrations (ug/g \pm 1 SE) in Sediments from ORNL Streams, First Quarter 1989

Location	n Concentration		
White Oak Creek Headwaters	3	0.02 ± 0.003	
Fifth Creek Outfall 362 Box	3	155.81 ± 131.57	
Fifth Creek Below Outfall 362	3	23.03 ± 2.83	
Fifth Creek Near Outfall 261	3	555.67 ± 310.38	
White Oak Creek Upstream of Fifth Creek	3	4.65 ± 1.79	
White Oak Creek Near Outfall 309	3	17.70 ± 6.31	
Northwest Tributary Upstream First Creek	3	0.27 ± 0.06	
First Creek Upstream of Northwest Tributary	3	1.37 ± 0.32	
White Oak Creek Downstream First Creek	3	2.81 ± 0.50	
White Oak Creek Upstream Melton Branch	3	1.35 ± 0.86	
Melton Branch Upstream of White Oak Creek	3	0.08 ± 0.01	
Melton Branch Two Upstream Weir	3	0.05 ± 0.0017	

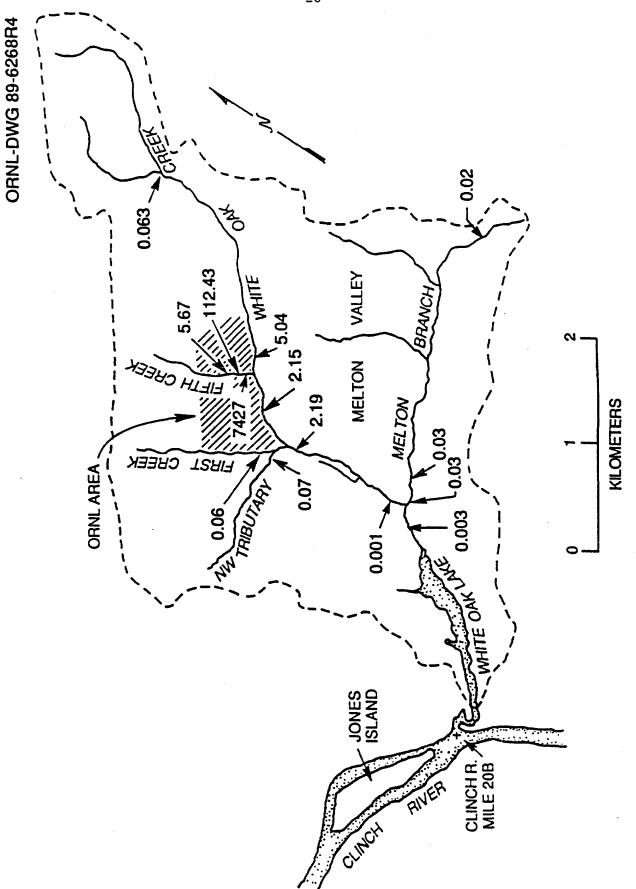
6.2.2 Fourth Quarter Sampling

During the Fourth Quarter the 12 stations sampled during the first quarter were sampled with the addition of samples from Melton Branch headwaters (an additional background location) and White Oak Creek downstream from the confluence with Melton Branch. A summary of the concentration data is presented in Fig. 5 and Table 5. Considering the variability between replications and within locations, the data were similar to the results of 1988 and first quarter The minimum concentration (0.003 ug/g) observed was at White Oak Creek downstream of the confluence with Melton Branch, while the maximum (7427 ug/g) was near Outfall 261. The major difference from the spring quarter (Table 4) was the decreased concentration (5.67 ug/g) noted downstream from the containment box below Outfall 362. The spring quarter concentration was 155.81 ug/g. During the fourth quarter, it was noted that the box did not have a significant accumulation of sediment, indicating the probability of washout by heavy stream flow following storm events. The mean concentration near Outfall 261 was much higher during the fourth quarter (7427 ug/g), where the between-replication error was 95% in contrast to a 55% between-replication error associated with the first quarter mean of 555.67 ug/g. The sediment data are considered important indicators in the selection of locations for continued water sampling sites.

6.2.3 Outfall 261 and Outfall 362

The monitoring report for 1988 (Taylor, 1989) identified a maximum sediment concentration of 4874 ug/g (top 5 cm) below Outfall 261. The discharge plume to Fifth Creek is 20 cm wide and 0.5 m long. The unusually high concentration suggested that a more detailed sample procedure include soils within depth profiles along the distance gradient to the creek. Samples were collected from 0-5, 5-10, 10-15, and 15-20 cm depths at 0, 0.25, and 0.5 m from Outfall 261. The concentrations nearest Fifth Creek indicate a dilution with distance, and the concentration similarity within the depth profile (0 to 20 cm) suggests a single release (spill) event (Fig. 6). The youngest deposition is nearest the surface, such that the greater concentrations noted between 5 and 15 cm deep indicate no new or recent deposition. The greatest concentration noted (21,500 ug/g) occurred within the top 5 cm at a distance of 0.25 m from the outfall. This may relate to physical characteristics (e.g., a depression) or more exchange sites at this locus.

The soil bulk density (1.4 g/cm^3) was determined gravimetrically and incorporated into calculations of the total soil mass present in each 5-cm-thick layer of the outfall to creek plume. Mercury concentrations from 0, 0.25, and 0.5 m (n = 3) along the plume were averaged to calculate the total mercury present. It is estimated that 52 g are present in the 0-5 cm layer, 3 g in the 5-10 cm layer, 5 g in the 10-15 cm layer, and 2 g in the 15-20 cm layer for a total of 62 g.



Locations in ORNL streams with excess mercury in sediments. Statistics are summarized in Table 5. Data represent fourth quarter 1989. Fig. 5.

Table 5. Summary of Mercury Concentrations (ug/g \pm 1 SE) in Sediments from ORNL Streams, Fourth Quarter 1989

Location	n	Concentration
White Oak Creek Headwaters	3	0.063 ± 0.004
Fifth Creek Outfall 362 Box	3	5.67 ± 0.54
Fifth Creek Below Outfall 362	3	112.43 ± 47.17
Fifth Creek Near Outfall 261	3	7427 ± 7071
White Oak Creek Upstream of Fifth Creek	3	5.04 ± 2.05
White Oak Creek Near Outfall 309	3	2.15 ± 0.68
Northwest Tributary Upstream First Creek	3	0.07 ± 0.01
First Creek Upstream of Northwest Tributary	3	0.06 ± 0.01
White Oak Creek Downstream First Creek	3	2.19 ± 0.26
White Oak Creek Upstream Melton Branch	3	1.001 ± 0.0003
Melton Branch Upstream White Oak Creek	3	0.03 ± 0.001
Melton Branch Two Upstream Weir	3	0.031 ± 0.004
Melton Branch Headwaters	3	0.015 ± 0.001
White Oak Creek Downstream Melton Branch	3	0.003 ± 0.001

MERCURY CONCENTRATIONS ALONG A DISTANCE GRADIENT TO A DEPTH OF 20 cm

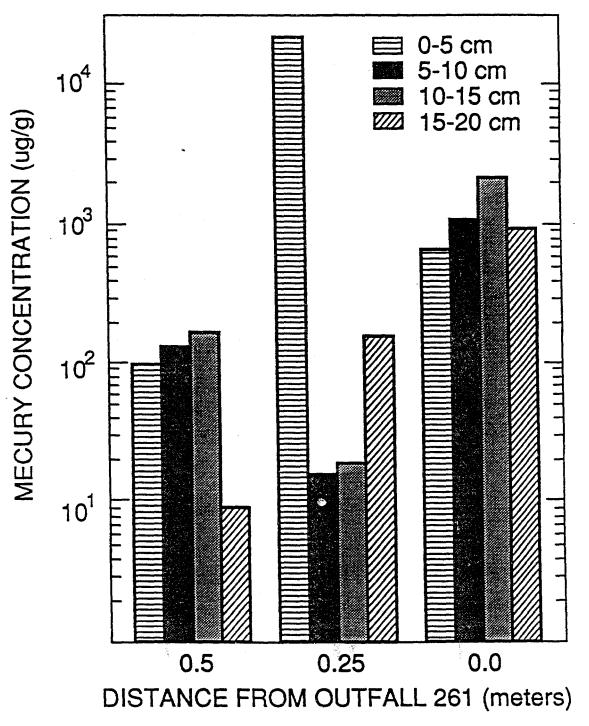


Fig. 6. Mercury concentrations in sediments along a distance gradient to a depth of 20 cm downstream of Outfall 261.

A containment box was placed beneath Outfall 362 from Buildings 4501 and 4505. The box contained sand and sized stones to reduce splash but permit any mercury from the outfall to settle. Occasionally, puddles of mercury are visible in the outfall pipe. The stones were removed along with leaves and debris, and the sand was sieved to collect any sediment. The box was left in place for one year before removal. Analysis of the sediment indicated a concentration of 147 ug/g of mercury. It is suggested that this procedure be repeated each month to confirm that surges of metallic mercury are not being discharged.

7.0 CONCLUSIONS AND RECOMMENDATIONS

The water chemistry data for the 1987 scoping survey, the 1988 annual mercury monitoring data, and the 1989 annual mercury monitoring data have clearly identified potential sources of mercury to ORNL streams. Sediment analyses identify pools of residual mercury as potential release sources during heavy runoff following storm events. The mercury monitoring plan to date has been a detailed program designed to identify, locate, and minimize all sources of mercury contamination to ORNL waters. The first two objectives have been accomplished, but the last item is less attainable since many sources are periodic spills. A criterion for reducing the water sampling efforts during 1990 is based on the absence of any evidence of mercury discharges relative to the State of Tennessee, Criteria for Water Conditions, Domestic Water Supply, Tennessee Rule 1200-4-3-.03, 1983. That guideline is 0.2 ug/L (0.2 ppb). As a conservative measure, it is proposed that any outfall source or stream location having mercury concentrations equivalent to 50% (0.1 ug/L) of the state rule during two or more sampling periods be continued as a sampling location. All others would be deleted as a cost-effective measure to attain the goals of the annual mercury monitoring plan. With these recommendations, 18 locations are recommended for annual sampling (Table 6).

On the other hand, mercury in sediments has the potential to be methylated and become bioavailable. Concentrations greater than 1 ug/g (A Conservative Estimate of Mercury in Surficial Materials in the Conterminous United States, Schacklette et al, 1971) have a potential to influence stream concentrations. Therefore, nine sediment locations are proposed for continued sampling. These locations are identified in Table 7. Sampling efforts should continue on a semiannual basis with no reductions in the number of replications per location.

It is recommended that a remedial action project be initiated to remove the soil/sediment plume from Outfall 261 to Fifth Creek. This would eliminate the area of highest mercury contamination. The catchment box below Outfall 362 should be removed on a monthly basis, the rocks, stones, and sand removed by fractional sieving, and the sediments (3 replicates) collected and analyzed for mercury.

It is a general conclusion that mercury contamination of ORNL waters is not yet an environmental concern. This conclusion is based on a good record of spill or accident events and three years of detailed water and sediment chemistry data.

Table 6. Outfalls Recommended for Continued Water Sampling by Stream or Outfall

1st Ck	5th Ck	White Oak Creek	Melton Branch	Miscellaneous
241				
341	• •			
	261		• • • •	
	363			
	367			
• •		106		
• •	• •		• • • •	
• •	• •	202		
	• •	207		
		222		
		301		
		302		
• •	• •	303	• • • • •	• • • •
• •	• •		• • • • •	• • • •
• •	• •	304	• • • •	
	. • •	305		
	• • .	X04		
		X07		
		X12		
	• •	7,12	X08	
• •	• •		AUU	White Oak Ck
• •	• •		• • • •	White Oak Ck Headwaters

Table 7. Location Recommendations for Continued Sediment Sampling by Stream or Outfall

1st Creek	5th Creek	White Oak Creek	Melton Branch
Upstream NW tributary	261	Headwaters	Headwaters
	362	309	• • • •
	• • •	Downstream 1st Creek	• • • •
• • • • •		Upstream 5th Creek	• • • •
		Upstream Melton Br	

					`
		• •		•	•
					* /
		V.			
					, ?
	·				
					ž .*
		•			
					٠,
		•			
•					

8.0 REFERENCES

- Personal file, W. A. Alexander, 1989, History of Chemical Spills at ORNL.
- U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C., "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods," EPA-SW-846 (1982).
- U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Office of Research and Development, Cincinnati, Ohio, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79/020 (1982).
- Letter T. W. Oakes to J. F. Wing, Department of Energy/Oak Ridge Operations, "Mercury in Soil and Sediment at ORNL," 1983a.
- Letter T. W. Oakes to J. F. Wing, Department of Energy/Oak Ridge Operations, "Mercury in Soil Samples at ORNL," 1983b.
- H. T. Shacklette et al., "Mercury Content of Surficial Materials in the Conterminous United States." U.S. Geological Survey Circular 644:1-5, 1971.
- Fred G. Taylor, Jr., "Mercury Assessment for Water and Sediment in Oak Ridge National Laboratory Streams, ORNL/M-713, Martin Marietta Energy Systems, Inc., Oak Ridge National Laboratory, March 1989; Emergency Response, Washington, D.C. "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods," EPA-SW-846.1989

INTERNAL DISTRIBUTION

- 1. D. F. Copeland
- 2. B. H. Freels
- 3. B. J. Hendrix
- 4. S. R. Lewis
- 5-7. J. B. Murphy
- 8-12. C. E. Nix
- 13-15. R. K. Owenby
 - 16. D. W. Parsons
 - 17. J. E. Powell
 - 18. P. S. Rohwer
 - 19. T. H. Row
 - 20. L. B. Ryon
 - 21. J. H. Swanks
- 22-31. F. G. Taylor
 - 32. C. K. Valentine
 - 33. J. B. Watson
 - 34. Central Research Library
- 35-36. ORNL Laboratory Records
 - 37. Laboratory Records-RC
 - 38. ORNL Patent Section

EXTERNAL DISTRIBUTION

- 39. Office of Assistant Manager for Energy Research and Development, U.S. Department of Energy Oak Ridge Operations, P. O. Box 2001, Oak Ridge, TN 37831-8731
- 40-49. Office of Scientific and Technical Information, U.S. Department of Energy, P. O. Box 462, Oak Ridge, TN 37831-8731
 - 50. B. J. Davis, Environmental Protection Division, U.S. Department of Energy - Oak Ridge Operations, P. O. Box 2001, Oak Ridge, TN 37831-8730
 - H. W. Hibbitts, Environmental Protection Division, U.S. Department of Energy - Oak Ridge Operations, P. O. Box 2001, Oak Ridge, TN 37831-8730